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On A. Raychaudhuri's paper "Electronic energy Bands in model three-dimensional lattices"

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Recently, Raychaudhuri published a paper on electronic energy bands in three-dimensional lattices[1]. The purpose of the present communication is twofold: (1) to point out that one of the simplifying assumptions made in I is invalid, and (2) to point out the possibility of obtaining a correct procedure which retains many of the advantages of RAYCHAUDHURI's approach.

In order to accomplish our objective, it is convenient to summarize the treatment employed in I. Essentially, the potential to be considered was taken as having the period of the lattice and as reducing in the vicinity of each lattice point, $\vec{r}_s$, to the "spherical square well":

$$\left.\begin{aligned} V(\vec{r}) = V_0 &= \text{constant}, \quad |\vec{r}-\vec{r}_s| < b \\ &= 0 \qquad\qquad\quad\ |\vec{r}-\vec{r}_s| > b \end{aligned}\right\} \tag{1}$$

where b is less than half the smallest interatomic distance. The relevant Schroedinger equation is then reduced to an integral equation over a unit cell involving the relevant Green's function. The relation

$$\int\limits_{|\vec{r}'|=b} \left[G(\vec{r},\vec{r}')\,\frac{\partial\psi(\vec{r}')}{\partial r'} - \psi(\vec{r}')\,\frac{\partial G(\vec{r},\vec{r}')}{\partial r'} \right] ds' = 0, \qquad r<b \tag{2}$$

is then established. In (2), $G(\vec{r},\vec{r}')$ is the Green's function for this problem and $r' = |\vec{r}'|$.

The solution of this equation is written in the form

$$\psi(\vec{r}) = \sum_{l,m} \beta_{lm}\, j_l(x_i r)\, Y_{lm}(\vartheta,\varphi) \tag{3}$$

where

$$x_i^2 = \frac{2m}{\hbar^2}(E+V_0) \tag{4}$$

β_{lm} are constants to be determined and $j_l(x_i r)$ and $Y_{lm}(\vartheta,\varphi)$ are respectively, l^{th} order spherical Bessel functions and normalized spherical

[1] RAYCHAUDHURI, A.: Z. Physik **148**, 435 (1957). Subsequently this paper will be referred to as I. We shall try to follow the notation in I as closely as possible.

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harmonics. The Green's function $G(\vec{r}, \vec{r}\,')$ is also expanded in terms of these functions and the expanded $G(\vec{r}, \vec{r}\,')$ and $\psi(\vec{r})$ are substituted into the integral to obtain the determinantal compatibility relation.

This relation turns out to be an infinite determinant, each term of which contains a summation over the lattice. At this point the assumption is introduced that, on the right hand side of (3), only $\beta_{00} \neq 0$; all other coefficients are assumed to vanish reducing the determinant to a single term. The following relation between the wave number $\vec{k}$ and the energy E is then readily obtained.

$$\sum_s{}' \frac{e^{i\vec{k}\cdot\vec{r}_s} e^{ikr_s}}{x r_s} = -\frac{e^{ixb}(ix\sin x_i b - x_i\cos x_i b)}{x\sin x_i b\cos xb - x_i\cos x_i b\sin xb} \tag{5}$$

where the prime over the summation symbol indicates that the term involving $\vec{r}_s = 0$ is to be omitted from the summation, and $r_s = |\vec{r}_s|$.

Physically, the objectionable point in this procedure is that the short range nature of the interactions between the electrons and the lattice ions is used to infer that all partial waves other than those of the s state disappear. In point of fact, the suppression of such higher waves would imply a strong interaction between an electron in one of these states and the lattice, and is contrary to the basic assumptions. The resulting difficulty can be easily understood by considering the case of the empty lattice. In this situation, the type of wave function considered reduces to a plane wave. Then all the terms in the spherical harmonic expansion are eliminated except for the first, and one obtains from equation (5) a restriction on the allowed energies — contrary to the physics of the situation. It may further be remarked that even in the case of a large V, the higher β's need not vanish. This follows because the corresponding partial waves are quite small inside the sphere of radius b even in the absence of a potential [in view of the strong r dependence of $j_l(x_i r)$] and hence, cannot be greatly affected by V.

As a final remark one may note that there is an approach to this problem suggested by Raychaudhuri's work which does not suffer from the above difficulty. Instead of dealing with the coefficients of the partial waves, one may consider the phase shifts. In this case, one can give physical arguments for expecting the phase shifts for all the partial waves to vanish except that for $l = 0$. This appears to be a physically acceptable approximation to employ in the current model and we are continuing an investigation of its application.

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